

Supporting information for:

Accurate Ab Initio Quantum Mechanics Simulations of Bi_2Se_3 and Bi_2Te_3 Topological Insulator Surfaces

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1 Spin-Orbit Coupling in CRYSTAL

We modified the CRYSTAL98 code to include spin-orbit coupling (SOC). We used the 1998 version because that is the last version for which source code was distributed. Here we sketch the modifications necessary to implement SOC. The Hamiltonian takes the form

$$H = T + U_{ECP} + U_{ee} + (\nabla V \times \vec{p}) \cdot \vec{\sigma},$$

where T is the kinetic energy operator, U_{ECP} is the sum of the pseudopotential and electron-nuclear operators, and U_{ee} is the electron-electron interaction. The last term is the spin-orbit operator, which includes an explicit spin dependence via the Pauli matrices $\vec{\sigma}$. This mixes the orbital and spin angular momenta. The wavefunction then takes the general form

$$|\Psi\rangle = |\psi_\alpha\rangle|\alpha\rangle + |\psi_\beta\rangle|\beta\rangle. \quad (1)$$

We must address both the SOC operator and the consequences of a wavefunction of this form. The SOC operator is straightforward to evaluate,^{S1} but equation (1) leads to many complications in treating symmetry, pseudopotentials, and the density matrix.

1.1 Symmetries

For computational efficiency, three types of symmetry are used: the crystal symmetry, the Hermitian property of operators, and time reversal symmetry.

1.1.1 Crystal Symmetry

Because the Hamiltonian explicitly includes spin in the spin-orbit operator, the symmetry operators of the space group of a given crystal must be applied to the spin coordinate. In other words, symmetry operator \mathcal{O} takes a function ϕ^σ with a given spin σ to a linear combination of α and β

spins for some new function $\tilde{\phi}$:

$$\mathcal{O}(\phi^\sigma) \rightarrow a\tilde{\phi}^\alpha + b\tilde{\phi}^\beta.$$

For example, imagine a rotation that takes a p_z orbital to a p_x orbital. With SOC, this is still the case, but we must now consider the initial p_z orbital and the final p_x as having α and β components. The α and β piece of the p_z orbital are each taken to some linear combination of the α and β pieces of the p_x orbital.

We can then think of space group operators as acting in two steps. In the first step, the space part (p_x, p_y, p_z , for instance) is transformed. This is already treated by the existing code, but we needed to apply these operators to the α and β piece of each orbital. In the second step, we have to rotate the spin parts. We can write this in general as

$$\begin{pmatrix} \tilde{\phi}^\alpha \\ \tilde{\phi}^\beta \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \phi^\alpha \\ \phi^\beta \end{pmatrix}$$

From this it is clear that we need a 2×2 representation of a space group operator. Therefore, it is necessary to use the homomorphism $SO(3) \rightarrow SU(2)$, which maps the orthogonal 3×3 spatial rotation to a unitary 2×2 matrix.

1.1.2 Hermitian Operators

For a Hermitian operator \mathcal{O} and states Ψ, Φ ,

$$\langle \Psi | \mathcal{O} | \Phi \rangle = \overline{\langle \Phi | \mathcal{O} | \Psi \rangle}.$$

In a system with translational symmetry, a basis function is associated with a unit cell \mathbf{R} . Because of the translational symmetry, we choose a unit cell $\mathbf{0}$ all other cells are referred to. Then,

$$\langle \Psi \mathbf{0} | \mathcal{O} | \Phi \mathbf{R} \rangle = \overline{\langle \Phi \mathbf{R} | \mathcal{O} | \Psi \mathbf{0} \rangle},$$

or, translating the entire system by \mathbf{R} ,

$$\langle \Psi \mathbf{0} | \mathcal{O} | \Phi \mathbf{R} \rangle = \overline{\langle \Phi \mathbf{0} | \mathcal{O} | \Psi - \mathbf{R} \rangle}. \quad (2)$$

In k-space,

$$\langle \Psi k | \mathcal{O} | \Phi k \rangle = \overline{\langle \Phi k | \mathcal{O} | \Psi k \rangle}. \quad (3)$$

From now on, we'll drop the $\mathbf{0}$.

1.1.3 Time Reversal

Time reversal symmetry says

$$\langle \Psi | \mathcal{O} | \Phi \rangle = \langle T \Phi | \mathcal{O} | T \Psi \rangle,$$

where T is the anti-unitary time reversal operator. For a periodic system, we have

$$\langle \Psi \mathbf{0} | \mathcal{O} | \Phi \mathbf{R} \rangle = \langle T \Phi \mathbf{R} | \mathcal{O} | T \Psi \mathbf{0} \rangle = \langle T \Psi \mathbf{0} | \mathcal{O} | T \Phi - \mathbf{R} \rangle. \quad (4)$$

The time reversal operator has no effect on the real space vector \mathbf{R} . However, time reversal negates momentum, so in k-space we have

$$\langle \Psi k | \mathcal{O} | \Phi k \rangle = \langle T \Phi - k | \mathcal{O} | T \Psi - k \rangle \quad (5)$$

The effect of T on the spin functions α and β is,

$$\begin{aligned} T\alpha &= \beta \\ T\beta &= -\alpha. \end{aligned}$$

1.2 Fock Matrix

Given a wavefunction of the form (1), the expectation of an operator \mathcal{O} is

$$\begin{aligned}
 \langle \Psi | \mathcal{O} | \Psi \rangle &= \langle \psi_\alpha \alpha + \psi_\beta \beta | \mathcal{O} | \psi_\alpha \alpha + \psi_\beta \beta \rangle \\
 &= \langle \psi_\alpha \alpha | \mathcal{O} | \psi_\alpha \alpha \rangle + \langle \psi_\beta \beta | \mathcal{O} | \psi_\beta \beta \rangle \\
 &+ \langle \psi_\alpha \alpha | \mathcal{O} | \psi_\beta \beta \rangle + \langle \psi_\beta \beta | \mathcal{O} | \psi_\alpha \alpha \rangle \\
 &\equiv \mathcal{O}^{\alpha\alpha} + \mathcal{O}^{\beta\beta} + \mathcal{O}^{\alpha\beta} + \mathcal{O}^{\beta\alpha}.
 \end{aligned}$$

If \mathcal{O} is independent of spin, like the Fock operator in the non-relativistic unrestricted Hartree-Fock approach, then the orthogonality of $|\alpha\rangle$ and $|\beta\rangle$ cause $\mathcal{O}^{\alpha\beta}$ and $\mathcal{O}^{\beta\alpha}$ to vanish. Even with SOC, this is still the case for the kinetic energy and electron-nuclear operators, so no modifications are required for these.

However, as discussed below, the pseudopotential and exchange operators can have non-zero $\alpha\beta$ and $\beta\alpha$ contributions. Consequently, instead of diagonalizing two separate Fock matrices F_α and F_β , each with $N \times N$ elements (where N is the number of basis functions), we must diagonalize one Fock matrix with $2N \times 2N$ entries having the form

$$\begin{pmatrix} F^{\alpha\alpha} & F^{\alpha\beta} \\ F^{\beta\alpha} & F^{\beta\beta} \end{pmatrix}.$$

1.2.1 Pseudopotential

Without spin-orbit coupling, the form of the pseudopotential is

$$U(r) = U_{L+1}(r) + \sum_{l=0}^L [U_l(r) - U_{L+1}(r)] \sum_{m=-l}^l |lm\rangle \langle lm|,$$

where L is the largest angular momentum in the core, and the U_l 's are expressed most commonly by a sum of gaussians. When spin-orbit coupling is included, l is not a good quantum number, and

we must instead project onto $|lsjm_j\rangle$, with $s = \frac{1}{2}$. Thus, the pseudopotential becomes

$$U(r) = U_{L+1}(r) + \sum_{l=0}^L \sum_{j=|l-\frac{1}{2}|}^{l+\frac{1}{2}} [U_l(r) - U_{L+1}(r)] \sum_{m_j=-j}^j |lsjm_j\rangle \langle lsjm_j|.$$

This can be rewritten in terms of projections onto $|lm\rangle$ via the Clebsch-Gordon coefficients:

$$U(r) = U_{L+1}(r) + \sum_{l=0}^L \sum_j [U_l(r) - U_{L+1}(r)] \sum_{m_j, m_l, m_s} \langle lsm_l m_s | lsjm_j \rangle |lm_l\rangle |sm_s\rangle.$$

By explicitly writing the sum over m_s and substituting the Clebsch-Gordon coefficients, we find the pseudopotential operator consists of $\alpha\alpha$, $\beta\beta$, $\alpha\beta$, and $\beta\alpha$ pieces. Details of evaluating the pseudopotential integrals were discussed by McMurchie and Davidson.^{S2}

Implementing fully relativistic pseudopotentials required a complete overhaul of the pseudopotential routines in the code. In fact, the pseudopotential integral routine was completely rewritten, since the extensive optimizations in the original code make it extremely difficult to modify in place.

1.2.2 Two-Electron Operators

It is easy to show by substitution of (1) that the Coulomb operator needs no modification. However, we want to use a hybrid density functional, that is, we wish to include exact Hartree-Fock exchange. Upon inserting a wavefunction of the form in equation 1, we find that with SOC, we must evaluate “off-diagonal” exchange terms of the form (using chemist’s notation)

$$\begin{aligned} K_{\mu\nu}^{\alpha\beta} &= -\frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma}^{\alpha\beta} \left(\phi_\mu^\alpha \phi_\lambda^\alpha | \phi_\nu^\beta \phi_\sigma^\beta \right) \\ K_{\mu\nu}^{\beta\alpha} &= -\frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma}^{\beta\alpha} \left(\phi_\mu^\beta \phi_\lambda^\beta | \phi_\nu^\alpha \phi_\sigma^\alpha \right). \end{aligned}$$

Of course, in a periodic code where the exchange operator is computed in real space (as it is in CRYSTAL), the translational symmetry of an infinite crystal must be dealt with. That is, ϕ_μ is assumed to be in the origin cell, and the exchange operator must be evaluated for ϕ_ν in all unit

cells R_V . Furthermore, the summation over basis functions λ and σ must include summations over unit cells as well. In practice, these sums are truncated, but evaluating these sums is challenging.

1.3 Density Matrix

Using (1), the density operator becomes

$$\begin{aligned}
P &= |\Psi\rangle\langle\Psi| \\
&= (|\phi_\alpha\rangle|\alpha\rangle + |\phi_\beta\rangle|\beta\rangle)(\langle\phi_\alpha|\langle\alpha| + \langle\phi_\beta|\langle\beta|) \\
&= |\phi_\alpha\rangle\langle\phi_\alpha| \cdot |\alpha\rangle\langle\alpha| + |\phi_\beta\rangle\langle\phi_\beta| \cdot |\beta\rangle\langle\beta| \\
&+ |\phi_\alpha\rangle\langle\phi_\beta| \cdot |\alpha\rangle\langle\beta| + |\phi_\beta\rangle\langle\phi_\alpha| \cdot |\beta\rangle\langle\alpha| \\
&\equiv P^{\alpha\alpha} + P^{\beta\beta} + P^{\alpha\beta} + P^{\beta\alpha}
\end{aligned}$$

As with the pseudopotential and exchange operators, we must add contributions from alpha-beta and beta-alpha. In general, we need density matrix elements of the form

$$P_{\mu\nu}^{\sigma\sigma'}(k) = \sum_{\mu\nu} c_\mu^\sigma(k) \overline{c_\nu^{\sigma'}(k)},$$

where σ and σ' can be either α or β . Diagonalization of the Fock matrix at a given k -point returns eigenvectors composed of $c_\mu^\sigma(k)$, the complex weight of basis function μ with spin σ to the wavefunction at k .

The first N components of an eigenvector are the $c_\mu^\alpha(k)$; the second N components are the $c_\mu^\beta(k)$. In a UHF code, these can be treated independently. The code simply reads the eigenvector for α , makes the density matrix P^α , then repeats the process for β . However, with SOC, the α and β contributions to an eigenvector must be mixed to compute $P^{\alpha\beta}$ and $P^{\beta\alpha}$. Hence, the code must read both the α and β pieces, then compute all four blocks of the density matrix.

The code computes the Fock and density matrices for an irreducible wedge of the Brillouin

zone and uses the space group symmetry to sum over the Brillouin zone and form the real space density matrix. Thus, we needed to modify this part of the code as discussed in Section 1.1. In addition to the space group symmetry, the original code also used a combination of time reversal symmetry and the commutation of the Hamiltonian with S_z to further reduce the number of k-points it evaluated. Without spin-orbit, these symmetries allow the code to assume $P_{\mu\nu}(-k) = \overline{P_{\mu\nu}(k)}$. Since the density matrix is transformed to real space, the code can simply add the contributions from k and $-k$ with the appropriate phase factors. These are complex conjugates, and the code simply keeps $2\text{Re}(P_{\mu\nu}(k))$. With SOC, the Hamiltonian does not commute with S_z , and we can only use the symmetries discussed in Section 1.1. For example, time reversal symmetry and Hermiticity tells us $P_{\mu\nu}^{\alpha\beta}(k) = -\overline{P_{\mu\nu}^{\beta\alpha}(-k)}$. Because of this assumption, our modified code is only applicable to time-reversal-invariant systems, and cannot treat magnetism.

References

- (S1) McMurchie, L. E.; Davidson, E. R. *Journal of Computational Physics* **1978**, *26*, 218 – 231.
- (S2) McMurchie, L. E.; Davidson, E. R. *Journal of Computational Physics* **1981**, *44*, 289 – 301.

2 B3PW Band Structures of Slabs

Figures S1 and S2 show the 1-7QL band structures for Bi_2Te_3 and Bi_2Se_3 , respectively.

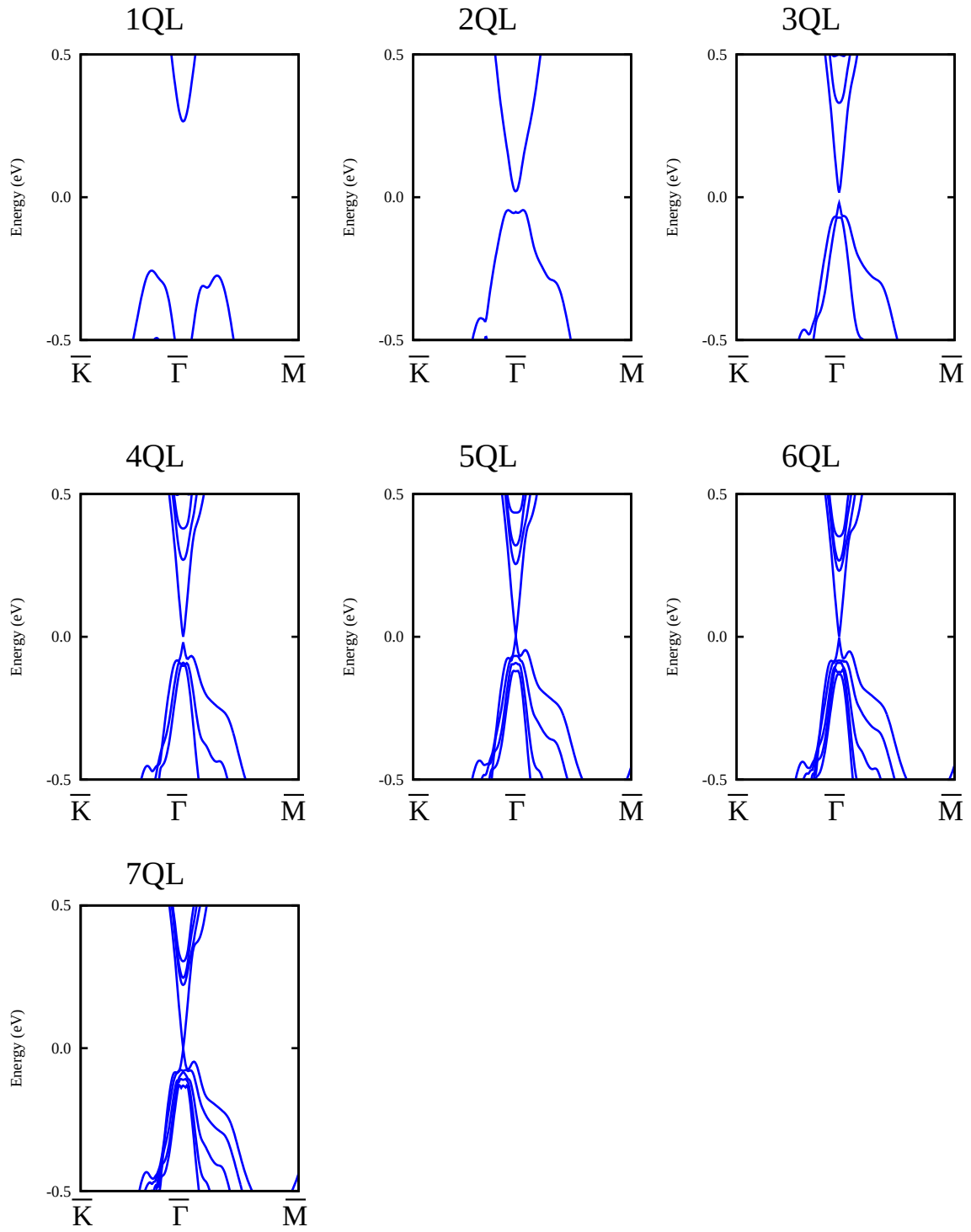


Figure S1: B3PW band structures of Bi_2Te_3 1-7QL slabs

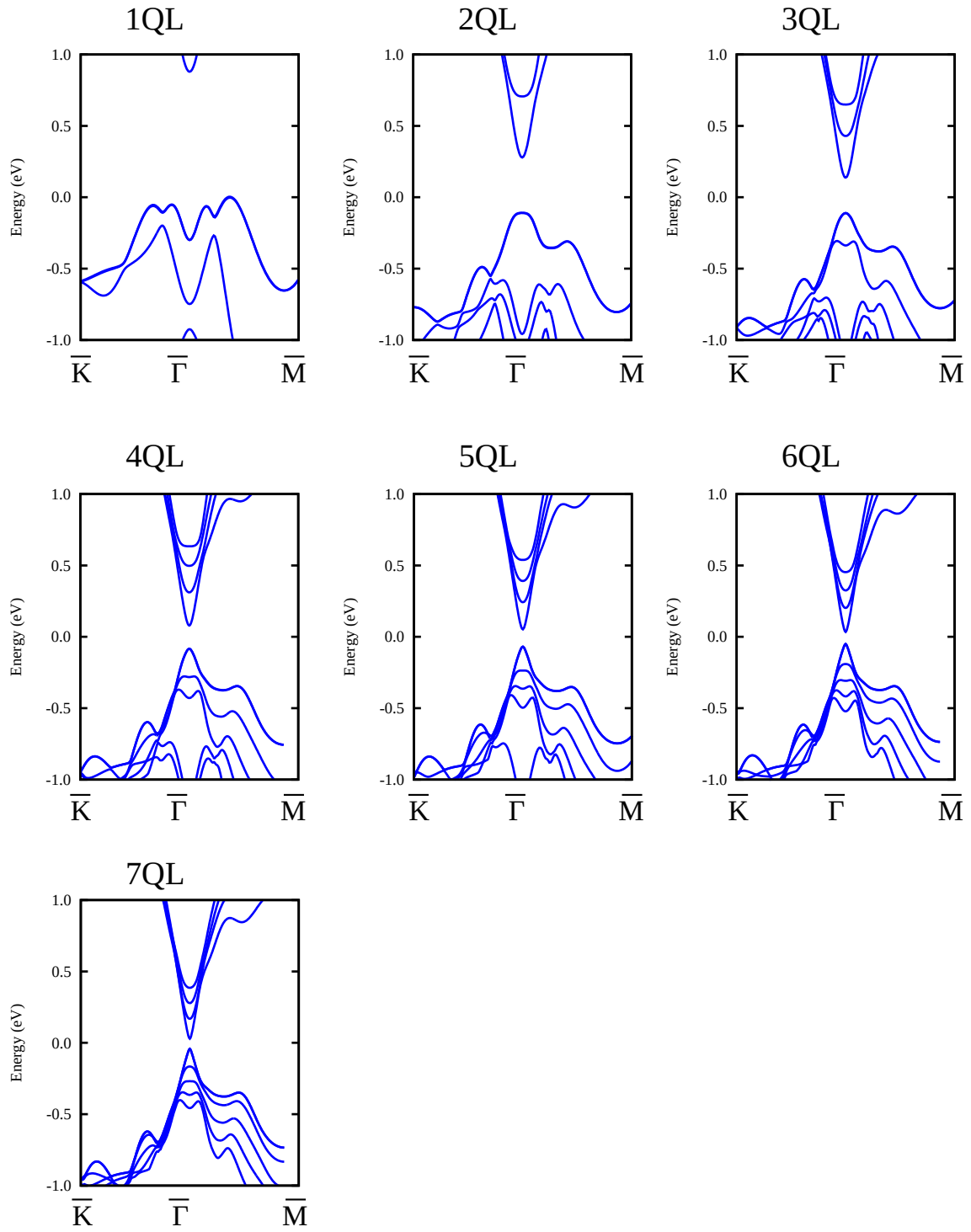


Figure S2: B3PW band structures of Bi_2Se_3 1-7QL slabs